

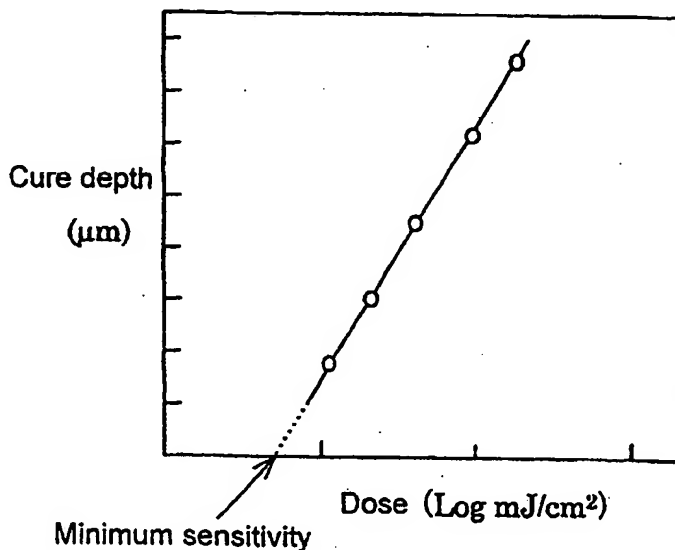
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(54) Title: PHOTO CURABLE LIQUID RESIN COMPOSITION AND PHOTOFABRICATED CURED PRODUCT



(57) Abstract

The invention provides a photo curable liquid resin composition which exhibits excellent photocurability and can produce a cured product having high mechanical strength, in particular, a photo curable liquid resin composition from which a three-dimensional object can be formed by photofabrication with high accuracy. More in particular, the photo curable liquid resin composition comprising: (A) a cationically polymerizable organic compound; (B) a cationic photoinitiator; and (C) a cationic photopolymerization photosensitizer comprising at least one compound comprising an N-substituted carbazole group.

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5 PHOTO CURABLE LIQUID RESIN COMPOSITION AND
 PHOTOFABRICATED CURED PRODUCT

 The present invention relates to a photo
10 curable liquid resin composition which excels in
 photocurability and can produce a cured product
 exhibiting superior mechanical characteristics. More
 particularly, the present invention relates to a photo
 curable liquid resin composition suitable as a coating
15 material for plastics, films, wood, ceramics, glass,
 optical quartz fibers for communication, papers,
 metals, cans for beverages, fibers, and the like,
 resins used for photofabrication of three-dimensional
 objects, sealing materials and adhesives for
20 semiconductors, filling agents, adhesives for optical
 materials, printing board materials, and the like. The
 resin composition exhibits high photocuring rate when
 exposed to various light sources such as a laser or a
 UV lamp or therefore is particularly suitable as a
25 resin used for photofabrication of three-dimensional
 objects.

 In recent years, stereophotofabrication for
 forming a three-dimensional object comprising
 integrally laminated cured resin layers formed by
30 repeating a step of forming the resin layer by
 selectively irradiating a photo curable liquid material
 (photo curable liquid resin composition) has been

proposed (see, Japanese Patent Applications Laid-open No. 247515/1985, No. 35966/1987, No. 101408/1987, and No. 24119/1993).

A typical example of such a photo-fabrication of three-dimensional objects is as follows.

A cured resin layer having a prescribed pattern is formed by selectively irradiating the liquid surface of a photo curable liquid resin composition using a UV laser and the like. The photo curable liquid resin composition equivalent to one layer is provided over this cured resin layer. This liquid surface is selectively irradiated to form a new cured resin layer integrally laminated on the previously-formed cured resin layer. This step is repeated for a prescribed number of times using the same or different irradiating patterns to form a three-dimensional object comprising integrally laminated cured resin layers. This photofabrication method has attracted attention because even a three-dimensional object having a complicated shape can be easily formed in a short period of time.

The following resin compositions (a)-(c) have been conventionally proposed as the photo curable liquid resin composition used for the photofabrication of three-dimensional objects.

- (a) A resin composition comprising a radically polymerizable organic compound such as a urethane (meth)acrylate, oligoester (meth)acrylate, epoxy (meth)acrylate, a combination of a thiol compound and an ene compound, and photosensitive polyimide (Japanese Patent Applications Laid-open No. 204915/1989, No.208305/1990, and No. 160013/1991).
- (b) A resin composition comprising a cationically polymerizable organic compound such as an epoxy

compound, cyclic ether compound, cyclic lactone compound, cyclic acetal compound, cyclic thioether compound, spiroorthoester compound, and vinyl ether compound (Japanese Patent Application Laid-open No. 213304/1989).

- 5 (c) A resin composition comprising a radically polymerizable organic compound and a cationically polymerizable organic compound (Japanese Patent Applications Laid-open No. 28261/1990, No. 75618/1990, and No. 228413/1994).

In order to achieve efficient photofabrication, the following characteristics are required for the photo curable liquid resin composition used for such a fabrication method:

- 15 (1) The composition has low viscosity for immediately forming a flat liquid surface;
(2) The composition is rapidly cured upon exposure to radiation;
(3) The composition does not swell when cured to
20 fabricate a three-dimensional object; and
(4) The composition exhibits minimum deformation due to cure shrinkage during photocuring, such as warping, indentation, and overhanging of the stretched part.

Three-dimensional objects produced by such
25 a photofabrication method are used as design models, prototypes for machine parts, and the like. In particular, when the three-dimensional object are used as prototypes for machine parts, such three-dimensional objects are required to have the following
30 characteristics.

- (5) The three-dimensional object can be subjected to microprocessing, in accordance with a plan with high accuracy.

(6) The three-dimensional object has sufficient mechanical strength and superior heat resistance under use conditions.

5 (7) The three-dimensional object exhibits stable mechanical characteristics with time.

However, conventional resin compositions cannot satisfy these requirements which have become more stringent day by day. A three-dimensional object prepared from these resin compositions by
10 photofabrication exhibits deformation with time such as warping, indentation, and overhanging of the stretched part due to the residual strain caused by cure shrinkage. When using the above resin composition (a) as the photo curable liquid resin composition, the
15 resulting three-dimensional object exhibits relatively superior mechanical characteristics but exhibits insufficient fabrication accuracy and inferior stability with time of the fabricated form, therefore further improvement has been demanded ("Seikei-Kakou",
20 Vol. 9, No. 5, pp. 330-335, 1997).

When the above resin composition (b) is used as the photo curable liquid resin composition, fabrication becomes inefficient due to poor curability. The three-dimensional shape is fabricated with
25 relatively high accuracy. However, such a three-dimensional object cannot be used under conditions where mechanical strength is required for a long period of time, because the mechanical characteristics of the resulting three-dimensional object deteriorate with
30 time, depending on the environment (temperature and humidity). Furthermore, since the three-dimensional object exhibits insufficient mechanical strength, in particular, insufficient toughness such as impact

resistance and bending durability, functional parts formed from the composition cannot stand up to practical use.

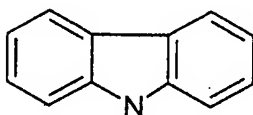
Because of the above situation, the resin composition (c) which comprises a radically polymerizable organic compound and a cationically polymerizable organic compound has been proposed. Curability is improved to some extent by using such a resin composition but is still insufficient, and the mechanical characteristics of the three-dimensional object are insufficient in practical use. In particular, curing rate and mechanical characteristics of the resin composition are insufficient in industrial scale manufacture using an Ar laser having a wavelength of 350 nm or more or i-lines from a high pressure mercury lamp as a light source.

The present invention has been achieved in view of the above situation. An object of the present invention is to provide a photo curable liquid resin composition which exhibits excellent photocurability and is capable of forming a cured product having superior mechanical characteristics. More particularly, an object of the present invention is to provide a photo curable liquid resin composition capable of rapidly forming a three-dimensional object by photofabrication with high accuracy. In particular, an object of the present invention is to provide a photo curable liquid resin composition exhibiting a high curing rate and superior mechanical characteristics upon exposure to near ultraviolet light having a wavelength of 350 nm or more.

Another object of the present invention is to provide a photofabricated cured product which

exhibits high mechanical strength, high dimensional accuracy, and the like and is suitable as prototypes for machine parts and the like.

In order to achieve the above objects, the present invention provides a photo curable liquid resin composition comprising (A) a cationically polymerizable organic compound, (B) a cationic photoinitiator, and (C) a cationic photopolymerization photosensitizer comprising at least one compound comprising an N-substituted carbazole group. A carbazole group is a group according to formula (1)



(1)

15

The invention furthermore proves a photofabricated cured product prepared by photopolymerization of the photo curable liquid resin composition of the present invention.

20

Cationically polymerizable organic compound (A)

As the cationically polymerizable organic compound (A) which constitutes the photo curable liquid resin composition of the present invention (hereinafter also referred to as "component (A)"), a compound which polymerizes by cationic photopolymerization can be used with no specific limitations. Examples of such a compound include cationically polymerizable monomers such as compounds containing a vinyl ether group, compounds containing a cyclic ether, lactones, cyclic

30

carbonates, cyclic imino ethers, and aromatic vinyl monomers. A compound containing cyclic ether referred to herein means a compound containing one or more groups consisting of an epoxy group such as a glycidyl group and a cyclohexene oxide group, an oxetanyl group (oxacyclobutyl group), oxacyclopentyl group, 3,4-epoxycyclohexyl group, and the like.

Of these compounds, compounds containing a glycidyl group, cyclohexene oxide group, or oxetanyl group are preferable in view of the curing rate and mechanical characteristics of the cured product.

The following compounds can be given as specific examples of a compound containing a glycidyl group:

bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol S diglycidyl ether, brominated bisphenol A diglycidyl ether, brominated bisphenol F diglycidyl ether, brominated bisphenol S diglycidyl ether, epoxy novolak resin, hydrogenated bisphenol A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, hydrogenated bisphenol S diglycidyl ether, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-meta-dioxane, bis(3,4-epoxycyclohexylmethyl)adipate, vinylcyclohexene oxide, 4-vinylepoxycyclohexane, bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate, 3,4-epoxy-6-methylcyclohexyl-3',4'-epoxy-6'-methylcyclohexanecarboxylate, methylenebis(3,4-epoxycyclohexane), dicyclopentadiene diepoxide, di(3,4-epoxycyclohexylmethyl) ether of ethylene glycol, ethylenebis(3,4-epoxycyclohexanecarboxylate), dioctylepoxyhexahydro phthalate,

di-2-ethylhexylepoxyhexahydro phthalate, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, neopentyl glycol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether,

5 polyethylene glycol diglycidyl ether, and polypropylene glycol diglycidyl ether; polydiglycidyl ethers of polyether polyols obtained by the addition of one or more alkylene oxides to an aliphatic polyhydric alcohol such as ethylene glycol, propylene glycol, and

10 glycerol; polydiglycidyl ethers of polyether polyols; diglycidyl esters of aliphatic long-chain dibasic acid; monodiglycidyl ethers of aliphatic higher alcohols; monodiglycidyl ethers of phenol, cresol, butyl phenol, or polyether alcohols obtained by the addition of

15 alkylene oxide to these compounds; glycidyl esters of higher aliphatic acids; epoxidated soybean oil; butylepoxystearate; octyl epoxystearate; epoxidated linseed oil; epoxidated polybutadiene; and the like. Of these, bisphenol A diglycidyl ether, bisphenol F

20 diglycidyl ether, hydrogenated bisphenol A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, neopentyl glycol diglycidyl ether,

25 polyethylene glycol diglycidyl ether, and polypropylene glycol diglycidyl ether are preferable.

As commercially available products which can be suitably used as the compound containing a glycidyl group, UVR-6216 (trade name, manufactured by

30 Union Carbide Corp.), Glycidole, AOEX24, Cyclomer A200 (trade name, manufactured by Daicel Chemical Industries, Ltd.), Epicoat 828, Epicoat 812, Epicoat 1031, Epicoat 872, Epicoat CT508 (trade name,

manufactured by Yuka-Shell K.K.), Epolite M-1230,
Epolite 40E, Epolite 100E, Epolite 200E, Epolite 400E,
Epolite 70P, Epolite 200P, Epolite 1500NP, Epolite
1600, Epolite 4000, Epolite FR-1500 (trade name,
5 manufactured by Kyoeisha Chemical Co., Ltd.), KRM-2400,
KRM-2410, KRM-2408, KRM-2490, KRM-2720, KRM-2750 (trade
name, manufactured by Asahi Denka Kogyo Co., Ltd.),
Araldite DY022 (trade name, manufactured by Nagase Ciba
Co., Ltd.), and the like can be given.

10 The following compounds can be given as
specific examples of a compound containing an
epoxycyclohexyl group:

3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane-
carboxylate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-
15 epoxy)cyclohexane-meta-dioxane, bis(3,4-epoxycyclo-
hexylmethyl)adipate, bis(3,4-epoxy-6-methylcyclo-
hexylmethyl)adipate, 3,4-epoxy-6-methylcyclohexyl-
3',4'-epoxy-6'-methylcyclohexanecarboxylate,
methylenebis(3,4-epoxycyclohexane), di(3,4-epoxycyclo-
20 hexylmethyl) ether of ethylene glycol, ethylenebis(3,4-
epoxycyclohexanecarboxylate, ϵ -caprolactone-modified
3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane-
carboxylate, trimethylcaprolactone-modified 3,4-
epoxycyclohexylmethyl-3',4'-epoxycyclohexane-
25 carboxylate, β -methyl- δ -valerolactone-modified 3,4-
epoxycyclohexylmethyl-3',4'-epoxycyclohexane-
carboxylate, and the like.

Of these, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclo-
hexanecarboxylate, bis(3,4-epoxycyclohexylmethyl)-
30 adipate, ϵ -caprolactone-modified 3,4-epoxycyclo-
hexylmethyl-3',4'-epoxycyclohexanecarboxylate,

trimethylcaprolactone-modified 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, and β -methyl- δ -valerolactone-modified 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate are preferable. Of these, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, and bis(3,4-epoxycyclohexylmethyl)adipate are particularly preferable.

As commercially available products of the compound containing an epoxycyclohexyl group, UVR-6100, UVR-6105, UVR-6110, UVR-6128, UVR-6200, UVR-6216 (trade name, manufactured by Union Carbide Corp.), Celoxide 2021, Celoxide 2021P, Celoxide 2081, Celoxide 2083, Celoxide 2085, Epolead GT-300, Epolead GT-301, Epolead GT-302, Epolead GT-400, Epolead 401, Epolead 403 (trade name, manufactured by Daicel Chemical Industries, Ltd.), KRM-2100, KRM-2110, KRM-2199 (trade name, manufactured by Asahi Denka Kogyo Co., Ltd.), and the like can be given.

The number of oxetanyl groups in the compound containing an oxetanyl group is 1-10, preferably 1-4, and more preferably 2.

The following compounds can be given as specific examples of the compound containing an oxetanyl group.

- 25 A compound containing one oxetanyl group:
- 3-ethyl-3-hydroxymethyloxetane,
 - 3-(metha)allyloxymethyl-3-ethyloxetane,
 - (3-ethyl-3-oxetanylmethoxy)methylbenzen,
 - 4-fluoro-[1-(3-ethyl-3-oxetanylmethoxy)methyl]benzene,
 - 30 4-methoxy-[1-(3-ethyl-3-oxetanylmethoxy)methyl]benzene,
 - [1-(3-ethyl-3-oxetanylmethoxy)ethyl]phenyl ether,
 - isobutoxymethyl(3-ethyl-3-oxetanylmethyl) ether,

isobornyloxyethyl(3-ethyl-3-oxetanylmethyl) ether,
isobornyl(3-ethyl-3-oxetanylmethyl) ether,
2-ethylhexyl(3-ethyl-3-oxetanylmethyl) ether,
ethyldiethylene glycol (3-ethyl-3-oxetanylmethyl)
5 ether, dicyclopentadiene(3-ethyl-3-oxetanylmethyl)
ether, dicyclopentenyl(3-ethyl-3-oxetanylmethyl) ether,
dicyclopentenyl(3-ethyl-3-oxetanylmethyl) ether,
tetrahydrofurfuryl(3-ethyl-3-oxetanylmethyl) ether,
10 tetrabromophenyl(3-ethyl-3-oxetanylmethyl) ether,
2-tetrabromophenoxyethyl(3-ethyl-3-oxetanylmethyl) ether,
tribromophenyl(3-ethyl-3-oxetanylmethyl) ether,
2-tribromophenoxyethyl(3-ethyl-3-oxetanylmethyl) ether,
2-hydroxyethyl(3-ethyl-3-oxetanylmethyl) ether,
2-hydroxypropyl(3-ethyl-3-oxetanylmethyl) ether,
15 butoxyethyl(3-ethyl-3-oxetanylmethyl) ether,
pentachlorophenyl(3-ethyl-3-oxetanylmethyl) ether,
pentabromophenyl(3-ethyl-3-oxetanylmethyl) ether,
bornyl(3-ethyl-3-oxetanylmethyl) ether, and the like.

20 Of these, (3-ethyl-3-oxetanylmethyl)-methylbenzen is preferable.

A compound containing two oxetanyl groups:
3,7-bis(3-oxetanyl)-5-oxa-nonane, 3,3'-(1,3-(2-methylenyl)propanediylbis(oxymethylene)bis-(3-ethyl-oxetane),
25 1,4-bis[(3-ethyl-3-oxetanylmethoxy)-methyl]benzene,
1,2-bis[(3-ethyl-3-oxetanylmethoxy)-methyl]ethane,
1,3-bis[(3-ethyl-3-oxetanylmethoxy)-methyl]propane,
ethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether,
dicyclopentenylbis(3-ethyl-3-oxetanylmethyl) ether,
30 triethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether,
tetraethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether,
tricyclodecanediyl-dimethylene(3-ethyl-3-oxetanylmethyl) ether,

trimethylolpropanetris(3-ethyl-3-oxetanylmethyl) ether,
1,4-bis(3-ethyl-3-oxetanylmethoxy)butane,
1,6-bis(3-ethyl-3-oxetanylmethoxy)hexane,
pentaerythritoltris(3-ethyl-3-oxetanylmethyl) ether,
5 pentaerythritoltetrakis(3-ethyl-3-oxetanylmethyl)
ether, polyethylene glycol bis(3-ethyl-3-oxetanyl-
methyl) ether, dipentaerythritolhexakis(3-ethyl-3-
oxetanylmethyl) ether, dipentaerythritolpentakis(3-
ethyl-3-oxetanylmethyl) ether, dipentaerythritol-
10 tetrakis(3-ethyl-3-oxetanylmethyl) ether, caprolactone-
modified dipentaerythritolhexakis(3-ethyl-3-
oxetanylmethyl) ether, caprolactone-modified
dipentaerythritolpentakis(3-ethyl-3-oxetanylmethyl)
ether, ditrimethylolpropanetetrakis(3-ethyl-3-
15 oxetanylmethyl) ether, EO-modified bisphenol A bis(3-
ethyl-3-oxetanylmethyl) ether, PO-modified bisphenol A
bis(3-ethyl-3-oxetanylmethyl) ether, EO-modified
hydrogenated bisphenol A bis(3-ethyl-3-oxetanylmethyl)
ether, PO-modified hydrogenated bisphenol A bis(3-
20 ethyl-3-oxetanylmethyl) ether, EO-modified bisphenol F
(3-ethyl-3-oxetanylmethyl) ether, and the like.

These compounds can be used individually or
in combinations of two or more.

The following compounds can be given as
25 specific examples of other cationically polymerizable
organic compounds which can be used as the component
(A):

trimethylene oxide; oxolanes such as tetrahydrofuran
and 2,3-dimethyltetrahydrofuran; cyclic acetals such as
30 trioxane, 1,3-dioxolane, and 1,3,6-trioxanecyclooctane;
cyclic lactones such as β -propylactone and ϵ -
caprolactone; thiiranes such as ethylene sulfide, 1,2-
propylene sulfide, and thioepichlorohydrin; thiethanes

such as 3,3-dimethylthiethane; vinyl ethers such as ethylene glycol divinyl ether, triethylene glycol divinyl ether, and trimethylolpropane trivinyl ether; spiroorthoesters obtained by the reaction of an epoxy
5 compound and lactone; ethylenically unsaturated compounds such as vinylcyclohexane, isobutylene, and polybutadiene; derivatives of these compounds; and the like.

The cationically polymerizable organic
10 compounds preferably used as the component (A) are a compound containing a glycidyl group such as neopentyl glycol diglycidyl ether, an epoxy compound having two or more alicyclic epoxy groups in the molecule such as 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane-
15 carboxylate and bis(3,4-epoxycyclohexylmethyl)adipate, and an oxetane compound having two or more oxetanyl groups in the molecule such as 1,4-bis[(3-ethyl-3-oxetanylmethoxy)ethyl]benzene. If the proportion of the compound containing a glycidyl group, oxetane compound,
20 or alicyclic epoxy compound, or combinations of these compounds is 50 wt% or more in the component (A), the resulting resin composition exhibits a high cationic polymerization rate (curing rate), thereby shortening the fabrication time. Moreover, deformation with time
25 of the resulting three-dimensional object can be reduced due to the small cure shrinkage of the resin composition.

Of these cationically polymerizable organic compounds, bisphenol A diglycidyl ether, bisphenol F
30 diglycidyl ether, hydrogenated bisphenol A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane-carboxylate, bis(3,4-epoxycyclohexylmethyl)adipate,

1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, neopentyl glycol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, neopentyl glycol diglycidyl ether, 5 polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, 3-ethyl-3-phenoxyethyl-oxetane, 1,4-bis[(3-ethyl-3-oxetanylmethoxy)-methyl]benzene, 1,2-bis[(3-ethyl-3-oxetanylmethoxy)methyl]ethane, trimethylolpropanetris(3-ethyl-10 3-oxetanylmethyl) ether, and the like are preferable.

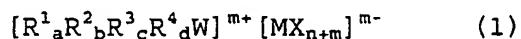
Component A preferably comprises one or more compounds having a molecular weight between 50-20,000. More preferred molecular weights are between 80-10,000.

15 The proportion of the component (A) in the photo curable liquid resin composition of the present invention is usually 60-99.9 wt%, preferably 70-99.5 wt%, and still more preferably 80-99.0 wt% for 100 wt% of the photo curable liquid resin composition (the 20 components (A), (B), and (C) in total). If the proportion is less than 60 wt%, the three-dimensional object formed from the resulting resin composition exhibits low dimensional accuracy and deformation with time. If the proportion is more than 99.9 wt%, the 25 resulting resin composition exhibits insufficient photocurability, thereby gives inefficient fabrication speed.

Cationic photoinitiator (B)

30 The cationic photoinitiator (B) which constitutes the photo curable liquid resin composition of the present invention (hereinafter also referred to as "component (B)") generates the substance which

initiates cationic polymerization of the component (A) upon exposure to energy rays such as light. Energy rays such as light used herein are visible rays, ultraviolet light, infrared radiation, X-rays, α -rays, β -rays, γ -rays, and the like. An onium salt having a structure shown by the following formula (1) can be given as a particularly preferable compound as the component (B):



10

wherein a cation is an onium ion; W represents S, Se, Te, P, As, Sb, Bi, O, I, Br, Cl, or $-N \equiv N$; R^1 , R^2 , R^3 , and R^4 individually represent organic groups; a, b, c, and d are integers from 0-3, provided that $(a + b + c + d)$ is equal to the valence of W; M represents a metal or metalloid which constitutes a center atom of the halide complex $[MX_{n+m}]$, such as B, P, As, Sb, Fe, Sn, Bi, Al, Ca, In, Ti, Zn, Sc, V, Cr, Mn, Co; X represents a halogen atom such as F, Cl, and Br; m represents a positive charge of a halide complex ion; and n is a valence of M. This onium salt generates a Lewis acid upon exposure to light.

As specific examples of the anion (MX_{n+m}) of the above formula (1), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), hexafluoroantimonate (SbF_6^-), hexafluoroarsenate (AsF_6^-), hexachloroantimonate ($SbCl_6^-$), and the like can be given.

An onium salt having an anion shown by the formula $[MX_n(OH)^-]$ can be used. An onium salt having other anions such as a perchloric acid ion (ClO_4^-), trifluoromethanesulfonic acid ion ($CF_3SO_3^-$), fluorosulfonic acid ion (FSO_3^-), toluenesulfonic acid

30

ion, trinitrobenzenesulfonic acid anion, and trinitrotoluenesulfonic acid anion can also be used.

Of these onium salts, aromatic onium salts are particularly effective as the component (B). Among
5 such aromatic onium salts, aromatic halonium salts disclosed in Japanese Patent Applications Laid-open No. 151996/1975, No.158680/1975, and the like, VIA group aromatic onium salts disclosed in Japanese Patent Applications Laid-open No. 151997/1975, No. 30899/1977,
10 No. 55420/1981, No. 125105/1980, and the like, VA group aromatic onium salts disclosed in Japanese Patent Application Laid-open No. 158698/1975, oxosulfoxonium salts disclosed in Japanese Patent Applications Laid-open No. 8428/1981, No. 149402/1981, No. 192429/1982,
15 and the like, aromatic diazonium salts disclosed in Japanese Patent Application Laid-open No. 17040/1974 and the like, thiopyrylium salts disclosed in U.S. Patent No. 4,139,655 and the like are preferable.

Iron/allene complex initiators, aluminum
20 complex/photolysis silicon compound initiators, and the like can also be given as examples.

As commercially available products of the cationic photoinitiator suitably used as the component (B), UVI-6950, UVI-6970, UVI-6974, UVI-6990 (trade
25 name, manufactured by Union Carbide Corp.), Adekaoptomer SP-150, SP-151, SP-170, SP-171 (trade name, manufactured by Asahi Denka Kogyo K.K.), Irgacure 261 (trade name, manufactured by Ciba Specialty Chemicals Co., Ltd.), CI-2481, CI-2624, CI-2639, CI-
30 2064 (trade name, manufactured by Nippon Soda Co., Ltd.), CD-1010, CD-1011, CD-1012 (trade name, manufactured by Sartomer), DTS-102, DTS-103, NAT-103, NDS-103, TPS-103, MDS-103, MPI-103, BBI-103 (trade

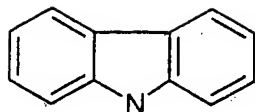
name, manufactured by Midori Chemical Co., Ltd.), PCI-061T, PCI-062T, PCI-020T, PCI-022T (trade name, manufactured by Nippon Kayaku Co., Ltd.), and the like can be given. Of these, use of UVI-6970, UVI-6974, Adekaoptomer SP-170, SP-171, CD-1012, MPI-103 is particularly preferable since the resin composition can be provided with high photocuring sensitivity.

These cationic photoinitiators can be used individually or in combinations of two or more as the component (B).

The proportion of the component (B) in the photo curable liquid resin composition of the present invention is usually 0.1-20 wt%, preferably 0.2-15 wt%, and still more preferably 0.3-10 wt% for 100 wt% of the photo curable liquid resin composition (the components (A), (B), and (C) in total). If the proportion is less than 0.1 wt%, the resulting resin composition exhibits insufficient photocurability, whereby a three-dimensional object having sufficient mechanical strength can not be formed. If the proportion is more than 10 wt%, controlling of the cure depth becomes difficult in photofabrication of the resin composition due to insufficient light transmittance, whereby fabrication accuracy of the resulting three-dimensional object tends to lower.

Cationic photopolymerization photosensitizer (C)

The cationic photopolymerization photosensitizer (C) used in the photo curable liquid resin composition of the present invention (hereinafter also referred to as "component (C)") comprises at least one N-substituted carbazole group. A carbazole group is a group with the formula (1)



(1)

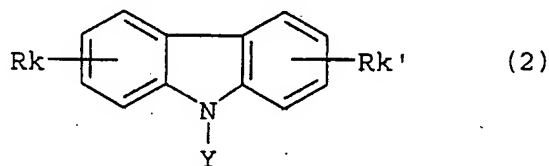
5 Compound C preferably is a compound comprising one or more, more preferably one to ten substituted carbazole groups, more in particular one or two substituted carbazole groups.

10 Compound C preferably does not comprise groups that neutralize acids. Hence the carbazole nitrogen should be substituted with an organic group such as for example an alkyl, alkenyl or aryl comprising organic group.

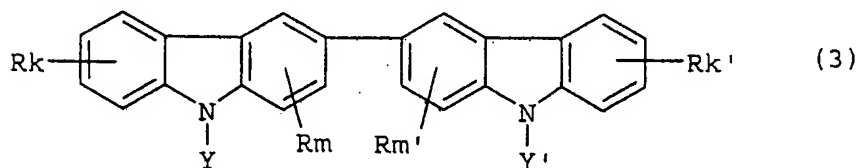
15 Compound C preferably has a molecular weight 180 or higher. Generally, the molecular weight will be lower than 2000, preferably lower than 1000.

The compound C having the at least one substituted carbazole group preferable is a compound shown by the following formula (2) or (3):

20



(2)



(3)

wherein R independently represents a fluorine atom, chlorine atom, bromine atom, a hydroxyl group, mercapto group, nitro group, or a C₁-C₁₉ monovalent organic group, k and k' independently represent integers from 0-4, m and m' independently represent integers from 0-2, and Y and Y' independently represent a C₁-C₁₈ monovalent organic group. Each substituent is described below.

Each R independently represents fluorine atom, chlorine atom, bromine atom, a hydroxyl group, mercapto group, nitro group, or a C₁-C₁₉ monovalent organic group, as mentioned above.

As examples of the C₁-C₁₉ monovalent organic group, a linear, branched, or cyclic C₁-C₁₈ alkyl group; linear, branched, or cyclic C₂-C₁₈ alkenyl group; monocyclic or condensed polycyclic C₆-C₁₈ aryl group; monocyclic or condensed polycyclic C₇-C₁₈ arylalkyl group; linear, branched, or cyclic C₁-C₁₈ alkoxyl group; monocyclic or condensed polycyclic C₆-C₁₈ aryloxy group; linear, branched, or cyclic C₁-C₁₈ aliphatic group; monocyclic or condensed aromatic C₇-C₁₉ acyl group; linear, branched, or cyclic C₂-C₁₉ alkoxycarbonyl group; and monocyclic or condensed polycyclic C₇-C₁₉ aryloxy-carbonyl group can be given. These organic groups can be replaced by a fluorine atom, chlorine atom, bromine atom, a hydroxyl group, carboxyl group, mercapto group, cyano group, or nitro group. In the formula (2) and (3), each Y independently represents a C₁-C₁₈ monovalent organic group. For example, a linear, branched, or cyclic C₁-C₁₈ alkyl group; linear, branched, or cyclic C₂-C₁₈ alkenyl group; and monocyclic or condensed polycyclic C₆-C₁₈ aryl group can be given as examples.

Specific examples of the linear, branched, or cyclic C₁-C₁₈ alkyl group which can be replaced by a fluorine atom, chlorine atom, bromine atom, a hydroxyl group, carboxyl group, mercapto group, cyano group, or nitro group include a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, sec-butyl group, t-butyl group, n-pentyl group, i-pentyl group, cyclopentyl group, hexyl group, cyclohexyl group, heptyl group, cyclopentyl group, octyl group, nonyl group, decyl group, dodecyl group, tetradecyl group, octadecyl group, fluoromethyl group, chloromethyl group, trifluoromethyl group, carboxymethyl group, mercaptomethyl group, cyanomethyl group, nitromethyl group, azidemethyl group, and the like.

Specific examples of the linear, branched, or cyclic C₂-C₁₈ alkenyl group which can be replaced by a fluorine atom, chlorine atom, bromine atom, a hydroxyl group, carboxyl group, mercapto group, cyano group, or nitro group include a vinyl group, propenyl group (allyl group), isopropenyl group, butenyl group, 2-methyl-1-propenyl group, 2-methylallyl group, hexenyl group, cyclohexenyl group, 1-octenyl group, 1-cyclohexenyl group, trifluoroethenyl group, 1-chloroethenyl group, 4-hydroxy-1-butenyl group, and the like.

Specific examples of the monocyclic or condensed polycyclic C₆-C₁₈ aryl group which can be replaced by a fluorine atom, chlorine atom, bromine atom, a hydroxyl group, carboxyl group, mercapto group, cyano group, or nitro group include a phenyl group, tolyl group, xylyl group, coumaryl group, mesityl group, 1-naphthyl group, 2-naphthyl group, 1-pyrenyl group, p-cumenyl group, o-fluorophenyl group, p-

mercaptophenyl group, p-cyanophenyl group, and the like.

Specific examples of the monocyclic or condensed polycyclic C₇-C₁₈ arylalkyl group which can be replaced by a fluorine atom, chlorine atom, bromine atom, a hydroxyl group, carboxyl group, mercapto group, cyano group, or nitro group include a benzyl group, p-tolylmethyl group, 2-naphthylmethyl group, o-fluorobenzyl group, p-hydroxybenzyl group, phenethyl group, styryl group, cinnamyl group, and the like.

Specific examples of the linear, branched, or cyclic C₂-C₁₈ alkoxyl group which can be replaced by a fluorine atom, chlorine atom, bromine atom, a hydroxyl group, carboxyl group, mercapto group, cyano group, or nitro group include a methoxy group, ethoxy group, propoxy group, isopropoxy group, butoxy group, pentyloxy group, cyclohexyloxy group, octyloxy group, fluoromethoxy group, chloromethoxy group, trifluoromethoxy group, hydroxymethoxy group, carboxymethoxy group, mercaptomethoxy group, cyanomethoxy group, and the like.

Specific examples of the monocyclic or condensed polycyclic C₆-C₁₈ aryloxy group which can be replaced by a fluorine atom, chlorine atom, bromine atom, a hydroxyl group, carboxyl group, mercapto group, cyano group, or nitro group include a phenoxy group, 1-naphthoxy group, 2-naphthoxy group, 5-naphthacenyl groups, 1-indenyloxy group, o-tolyloxy group, 2,3-xylyloxy group, p-cumenyloxy group, p-cyclohexylphenoxy group, o-fluorophenoxy group, o-mercaptophenoxy group, and the like.

Specific examples of the linear, branched, or cyclic C₁-C₁₈ aliphatic group or a monocyclic or

condensed polycyclic C₇-C₁₉ aromatic acyl group which can be replaced by a fluorine atom, chlorine atom, bromine atom, a hydroxyl group, carboxyl group, mercapto group, cyano group, or nitro group include a
5 formyl group, acetyl group, propionyl group, butyryl group, isobutyryl group, isovaleryl group, pivaloyl group, hexanoyl group, lauroyl group, palmitoyl group, stearoyl group, cyclohexylcarbonyl group, benzoyl group, 1-naphthoyl group, 2-naphthoyl group,
10 chloroacetyl group, hydroxyacetyl group, cyanoacetyl group, and the like.

Specific examples of the linear, branched, or cyclic C₂-C₁₉ alkoxy carbonyl group which can be replaced by a fluorine atom, chlorine atom, bromine
15 atom, a hydroxyl group, carboxyl group, mercapto group, cyano group, or nitro group include a methoxycarbonyl group, ethoxycarbonyl group, propoxycarbonyl group, butoxycarbonyl group, isopropoxycarbonyl group, t-butoxycarbonyl group, fluoromethoxycarbonyl group,
20 chloromethoxycarbonyl group, carbomethoxycarbonyl group, cyanomethoxycarbonyl group, nitromethoxycarbonyl group, and the like.

Specific examples of the monocyclic or condensed polycyclic C₇-C₁₉ aryloxy carbonyl group which
25 can be replaced by a fluorine atom, chlorine atom, bromine atom, a hydroxyl group, carboxyl group, mercapto group, cyano group, or nitro group include a phenoxycarbonyl group, 1-naphthyloxy carbonyl group, 2-naphthyloxy carbonyl group, tolyloxy carbonyl group,
30 xylyloxy carbonyl group, chlorophenoxycarbonyl group, p-hydroxyphenoxycarbonyl group, m-azidephenoxycarbonyl group, and the like.

Of these, a methyl group, ethyl group, n-propyl group, i-propyl group, t-butyl group, formyl group, acetyl group, propionyl group, benzoyl group, naphthoyl group, and the like are preferable as the
5 substituent R. Use of a basic group such as an amino group and alkyl-substituted amino group as the substituent R is undesirable since the acid generated by irradiation is neutralized by such a group, whereby cationic polymerization activity is lowered. The
10 numbers k and k' of the substituent R, which may be integers from 0-4, are preferably 0, 1, or 2 in view of the sensitization effect of the photosensitizer. If k and k' exceed 2, the sensitization effect may be insufficient.

15 In the formulas (2) and (3), Y and Y' independently represent a C₁-C₁₈ monovalent organic group. For example, a linear, branched, or cyclic C₁-C₁₈ alkyl group; linear, branched, or cyclic C₂-C₁₈ alkenyl group; and monocyclic or condensed polycyclic C₆-C₁₈
20 aryl group can be given as examples. Examples of the linear, branched, or cyclic C₁-C₁₈ alkyl group include a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, sec-butyl group, t-butyl group, n-pentyl group, i-pentyl group,
25 cyclopentyl group, hexyl group, cyclohexyl group, heptyl group, cyclopentyl group, octyl group, nonyl group, decyl group, dodecyl group, tetradecyl group, octadecyl group, and the like.

Examples of the linear, branched, or cyclic
30 C₂-C₁₈ alkenyl group include a vinyl group, propenyl group (allyl group), isopropenyl group, butenyl group, 2-methyl-1-propenyl group, 2-methylallyl group, hexenyl

group, cyclohexenyl group, 1-octenyl group, 1-cyclohexenyl group, and the like.

Examples of the monocyclic or condensed polycyclic C₆-C₁₈ aryl group include a phenyl group, 5 tolyl group, xylyl group, coumaryl group, mesityl group, 1-naphthyl group, 2-naphthyl group, 1-pyrenyl group, p-cumenyl group, and the like.

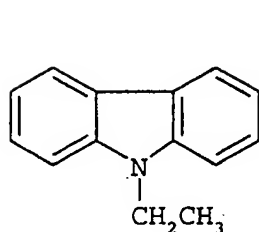
Y and Y' in the carbazole compound used in the present invention must not be hydrogen atoms, since 10 the carbazole compound neutralizes acids generated by irradiation to hinder cationic polymerization. If Y and Y' are C₁-C₁₈ monovalent organic groups, the carbazole compounds only provide the sensitization effect without hindering cationic polymerization.

15 Of these, a methyl group, ethyl group, vinyl group, and the like are preferable as the substituents Y and Y'.

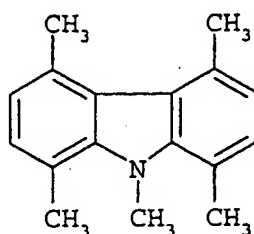
As examples of the carbazole compound which can be suitably used as the cationic 20 photopolymerization photosensitizer of the component (C) of the present invention, N-methylcarbazole, N-ethylcarbazole (hereinafter may be abbreviated as "NEC"), N-propylcarbazole, N-butylcarbazole, N-vinylcarbazole, 1,3,6,8,9-pentamethylcarbazole, 25 1,4,5,8,9-pentamethylcarbazole (hereinafter may be abbreviated as "NMPC"), 3-formyl-N-ethylcarbazole, N-phenylcarbazole, N-ethyl-3,6-bis(benzoyl)-carbazole (hereinafter may be abbreviated as "NEBC"), and 9,9'-diethyl-3,3'-dicarbazole (hereinafter may be 30 abbreviated as "NEDC") can be given. These carbazole compounds can be used either individually or in combinations of two or more. Chemical formulas for NEC,

NMPC, NEBC, and NEDC, which are preferable examples of the carbazole compound, are shown below.

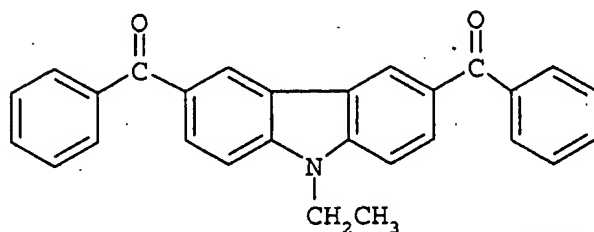
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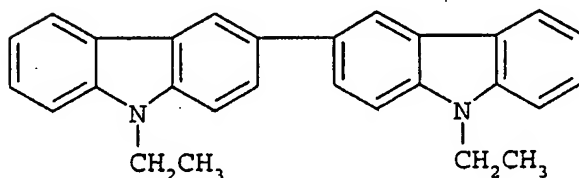
NEC



NMPC



NEBC



NEDC

Of these carbazole compounds, NEDC, NEBC, and NMPC are particularly preferable.

These carbazole compounds can be used
10 either individually or in combinations of two or more as the component (C).

The proportion of the component (C) in the photo curable liquid resin composition of the present invention is usually 0.001-20 wt% , preferably 0.01-15
15 wt%, and still more preferably 0.05-10 wt% for 100 wt%

of the photo curable liquid resin composition (the components (A), (B), and (C) in total). If the proportion is less than 0.001 wt%, improvement of the photocuring rate by the addition of the component (C) may be insufficient and the resulting three-dimensional object may exhibit inferior mechanical strength. If the proportion is more than 20 wt%, time required for producing a fabricated object with high accuracy may become longer due to the insufficient cure depth at the time of photofabrication.

Optional component

In the photo curable liquid resin composition of the present invention, radically polymerizable organic compounds, radical photoinitiators, form stabilizing agents, polymerization inhibitors, leveling agents, wettability improvers, surfactants, plasticizers, UV absorbers, silane coupling agents, inorganic fillers, pigments, dyes, and the like can be added as optional components other than the essential components (components (A)-(C)) insofar as the effect of the present invention is not impaired.

As examples of radically polymerizable organic compounds, a monofunctional monomer having one ethylenically unsaturated bond in the molecule and a polyfunctional monomer having two or more ethylenically unsaturated bonds in the molecule can be given.

Examples of monofunctional monomers which can be suitably used as a monofunctional monomer having one ethylenically unsaturated bond in the molecule include isobutoxymethyl (meth)acrylamide, isobornyloxyethyl (meth)acrylate, isobornyl (meth)acrylate, 2-

ethylhexyl (meth)acrylate, ethyldiethylene glycol
(meth)acrylate, lauryl (meth)acrylate, dicyclo-
pentadiene (meth)acrylate, dicyclopentenylloxyethyl
(meth)acrylate, dicyclopentenyl (meth)acrylate, 2-
5 tetrachlorophenoxyethyl (meth)acrylate, tetrahydro-
furfuryl (meth)acrylate, tetrabromophenyl (meth)-
acrylate, 2-tetrabromophenoxyethyl (meth)acrylate, 2-
trichlorophenoxyethyl (meth)acrylate, tribromophenyl
(meth)acrylate, 2-tribromophenoxyethyl (meth)acrylate,
10 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl
(meth)acrylate, phenoxyethyl (meth)acrylate,
butoxyethyl (meth)acrylate, pentachlorophenyl
(meth)acrylate, pentabromophenyl (meth)acrylate,
polyethylene glycol mono(meth)acrylate, polypropylene
15 glycol mono(meth)acrylate, bornyl (meth)acrylate,
methyltriethylene diglycol (meth)acrylate, and the
like.

Examples of polyfunctional monomers which
can be suitably used as a polyfunctional monomer having
20 two or more ethylenically unsaturated bonds in the
molecule include ethylene glycol di(meth)acrylate,
dicyclopentenyl di(meth)acrylate, triethylene glycol
diacrylate, tetraethylene glycol di(meth)acrylate,
tricyclodecanediylldimethylene di(meth)acrylate,
25 trimethylolpropane tri (meth)acrylate, ethylene oxide
(hereinafter also referred to as "EO") modified
trimethylolpropane tri(meth)acrylate, propylene oxide
(hereinafter also referred to as "PO") modified
trimethylolpropane tri(meth)acrylate, tripropylene
30 glycol di(meth)acrylate, neopentyl glycol di(meth)-
acrylate, both-terminal (meth)acrylic acid adduct of
bisphenol A diglycidyl ether, 1,4-butanediol
di(meth)acrylate, 1,6-hexanediol di(meth)acrylate,

pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, polyester di(meth)acrylate, polyethylene glycol di(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)-
5 acrylate, dipentaerythritol tetra(meth)acrylate, caprolactone-modified dipentaerythritol hexa(meth)-acrylate, caprolactone-modified dipentaerythritol penta(meth)acrylate, ditrimethylolpropane tetra(meth)-acrylate, EO-modified bisphenol A di(meth)acrylate, PO-
10 modified bisphenol A di(meth)acrylate, EO-modified hydrogenated bisphenol A di(meth)acrylate, PO-modified hydrogenated bisphenol A di(meth)acrylate, EO-modified bisphenol F di(meth)acrylate, (meth)acrylate of phenol novolak polyglycidyl ether, and the like.

15 Radical photoinitiators decompose upon exposure to energy rays such as light and generate radicals to initiate radical polymerization of radically polymerizable organic compounds.

Specific examples of such radical
20 photoinitiators include acetophenone, acetophenone benzyl ketal, anthraquinone, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, xanthone, 4-chloro-benzophenone, 1,1-dimethoxydeoxybenzoin, 3,3'-dimethyl-4-methoxybenzophenone, thioxanethone-type compounds,
25 2,4,6-trimethylbenzoyldiphenylphosphine oxide, bis(2,6-dimethoxybenzoyl-2,4,4-tri-methylpentyl-phosphine oxide, benzyl dimethyl ketal, 1-hydroxy-cyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, fluorenone, fluorene, benzaldehyde,
30 benzoin ethyl ether, benzoin propyl ether, benzophenone, 3-methylacetophenone, 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone (BTTB), combinations of BTTB and dyesensitizers such as xanthene,

thioxanthene, cumarin, and ketocumarin, and the like. Of these, benzyl dimethyl ketal, 1-hydroxycyclohexyl phenyl ketone, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, and the like are particularly preferable.

- 5 These radical photoinitiators can be used either individually or in combinations of two or more.

Form stabilizing agents have a function to prevent a three-dimensional object from deformation with time. Polyols having two or more, preferably three
10 or more, and still more preferably 3-6 hydroxyl groups in the molecule can be used as such form stabilizing agents.

As examples of form stabilizing agents, polyether polyols obtained by modifying polyhydric
15 alcohols having three or more hydroxyl groups such as trimethylolpropane, glycerol, pentaerythritol, sorbitol, sucrose, and quadrol with cyclic ether compounds such as ethylene oxide (EO), propylene oxide (PO), butylene oxide, and tetrahydrofuran can be given.
20 Specific examples include EO-modified trimethylolpropane, PO-modified trimethylolpropane, tetrahydrofuran-modified trimethylolpropane, EO-modified glycerol, PO-modified glycerol, tetrahydrofuran-modified glycerol, EO-modified
25 pentaerythritol, PO-modified pentaerythritol, tetrahydrofuran-modified pentaerythritol, EO-modified sorbitol, PO-modified sorbitol, EO-modified sucrose, PO-modified sucrose, EO-modified quadrol, polyoxyethylenediol, polyoxypropylenediol,
30 polyoxytetramethylenediol, polyoxybutylenediol, polyoxybutylene-oxyethylene copolymer diol, and the like. Of these, EO-modified trimethylolpropane, PO-

modified trimethylolpropane, PO-modified glycerol, and PO-modified sorbitol are preferable.

As examples of polymerization inhibitors, phenothiazine, 2,6-di-t-butyl-4-methylphenol, and the like can be given.

The photo curable liquid resin composition of the present invention is prepared by homogeneously mixing the components (A)-(C) and the above optional components, as required.

Viscosity (25°C) of the photo curable liquid resin composition is preferably 50-2,000 cps, and still more preferably 70-1,500 cps .

<Photofabrication of three-dimensional objects>

The photo curable liquid resin composition of the present invention is suitably used as photocurable liquid resin materials used for photofabrication of three-dimensional objects. Specifically, the photo curable liquid resin composition of the present invention is provided with the energy rays for curing by selectively irradiating with UV lights to produce a three-dimensional object having a desired shape.

There are no specific limitations to the means of selectively irradiating the photo curable liquid resin composition with UV light. For example, a means of irradiating the composition while scanning with laser beams or focused rays converged by lenses, mirrors, and the like, a means of irradiating the composition with unfocused rays via a mask having a phototransmission area with a specified pattern, a means of irradiating the composition via optical fibers corresponding to a specified pattern of a photo conductive material comprising bundled multiple optical

fibers, and the like can be employed. When using a mask, a mask which electrooptically forms a mask image consisting of a phototransmission area and a non-phototransmission area in accordance with a specified
5 pattern by the same concept as that of a liquid crystal display can be used. If the objective three-dimensional object has a minute part or high dimensional accuracy is required, a means of scanning with laser beams having a small spot diameter is preferably employed.

10 The irradiation surface (for example, scanning plane of the focused rays) of the resin composition in a container may be either the liquid surface or the surface in contact with the wall of the container. In this case, the resin composition can be
15 irradiated either directly or through the wall from the outside of the container.

 In photofabrication of three-dimensional objects, after curing a specific area of the resin composition, the cured layers are laminated by moving
20 the irradiation area of light (irradiation surface) from the cured area to the uncured area continuously or stepwise to form a desired three-dimensional shaped product. The irradiation area can be moved by, for example, moving a light source, the container for the
25 resin composition, or the cured area of the resin composition, or supplying additional resin composition to the container.

 A typical example of such a photofabrication is as follows. The resin composition is
30 provided on a support stage placed inside the container and able to move up and down by minutely lowering (submerging) the support stage to form a thin layer 1 of the resin composition. This thin layer 1 is

selectively irradiated to form a solid cured resin layer 1. The photo curable liquid resin composition is provided over this cured resin layer 1 to form a thin layer 2. This thin layer 2 is selectively irradiated to
5 form a cured resin layer 2 integrally laminated on the cured resin layer 1. This step is repeated for a prescribed number of times while either using the same or different irradiation patterns to obtain a three-dimensional object consisting of integrally laminated
10 cured resin layers (n).

The three-dimensional object thus obtained is removed from the container and washed as required after removing the unreacted resin composition remaining on the surface. As a detergent used in this
15 washing, alcohol-type organic solvents represented by alcohols such as isopropyl alcohol and ethyl alcohol; ketone-type organic solvents represented by acetone, ethyl acetate, and methyl ethyl ketone; aliphatic organic solvent represented by terpenes; and a heat
20 curable resin or photo curable liquid resin having low viscosity can be used.

When fabricating a three-dimensional object having surface smoothness, it is preferable to wash the surface of the three-dimensional object using a heat
25 curable or photo curable resin. In this case, a post-cure should be performed in accordance with the type of such a curable resin used for washing by exposure to heat or light. Since not only the resin on the surface but also the unreacted resin composition remaining
30 inside the three-dimensional object can be cured by the post-cure, it is preferable to perform the post-cure when washing with an organic solvent.

The three-dimensional object thus obtained exhibits excellent mechanical strength and high dimensional accuracy. The three-dimensional object excels in form stability and physical stability and
5 therefore is suitably used as a prototype for machine parts and the like.

Furthermore, in order to improve surface hardness and heat resistance of the three-dimensional object, heat curable or photo curable hard coating
10 materials are preferably provided after washing. Organic coating materials comprising acrylic resins, epoxy resins, silicone resin, and the like and inorganic hard coating can be used as such hard coating materials. These hard coating materials can be used
15 either individually or in combinations of two or more.

As described above, the composition of the present invention is useful for photofabrication of three-dimensional objects as well as a coating material for plastics, films, wood, ceramics, glass, optical
20 quartz fibers for communication, papers, metals, beverage cans, fibers, and the like, resins used in photofabrication of three-dimensional objects, sealing materials and adhesives for semiconductors, underfilling agents, adhesives for optical materials,
25 printing board materials, and the like since the cured products of the composition exhibit excellent mechanical characteristics and the like. In particular, when the composition of the present invention is used as a resin for photofabrication of three-dimensional
30 objects using a photofabrication apparatus with near ultraviolet light having a wavelength of 350 nm or more as a light source, a cured product exhibiting high

curing rate and a fabricated product exhibiting superior mechanical characteristics can be obtained.

Examples

- 5 The present invention will now be described in detail by way of examples, which should not be construed as limiting the present invention.

Example 1

- 10 A vessel equipped with a stirrer was charged with 64.5 wt% of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (manufactured by Union Carbide Corp., trade name: UVR-6110) (component A1) and 30 wt% of neopentyl glycol diglycidyl ether
15 (manufactured by Kyoeisha Chemical Co., Ltd., trade name: Epolite) (component A2) as cationically polymerizable organic compounds, 5.0 wt% of bis[4-(di(4-(2-hydroxyethyl)phenyl)sulfonio)phenyl]sulfide bishexafluoroantimonate (manufactured by Union Carbide
20 Corp., trade name: UVI-6970) (component B1) as a cationic photoinitiator, and 0.5 wt% of 9,9'-diethyl-3,3'-dicarbazole (NEDC) as a cationic photopolymerization photosensitizer (component C1) so that the total weight is 80 kg. The mixture was stirred
25 at 60°C for 3 hours to prepare a liquid resin composition (the resin composition of the present invention).

- Fabricability of the resulting resin composition was evaluated using a photofabrication
30 apparatus (manufactured by SONY Corp., trade name: Solid Creator JSC-2000, light source: Ar ion laser, wavelength: 351, 365 nm) according to the method described below. This resin composition exhibited

excellent curability. Cure depth and minimum sensitivity at a dose of 100 mJ/cm² of this resin composition were 300 μm and 16 mJ/cm², respectively. The resulting cured product exhibited a superior
5 Young's modulus of 190 kg/cm².

Examples 2-5

A vessel equipped with a stirrer was charged with the components as used in Example 1 according to the blending ratios shown in Table 1. The
10 mixture was stirred at 60°C for 3 hours to prepare liquid resin compositions. Fabricability of the resulting liquid compositions was evaluated using JSC-2000 in the same manner as in Example 1. The results
15 are shown in Table 1. These resin compositions exhibited excellent sensitivity and superior mechanical characteristics.

Comparative Example 1

20 According to the blending ratios shown in Table 1, a liquid resin composition was prepared in the same manner as in Example 1 except that a cationic photopolymerization photosensitizer was not used.

Fabricability of the resulting liquid
25 composition was evaluated using JSC-2000 in the same manner as in Example 1. This resin composition exhibited a cure depth of only 80μm and a low minimum sensitivity of 56 mJ/cm² at a dose of 100 mJ/cm².

Comparative Example 2

30 According to the blending ratios shown in Table 1, a liquid resin composition was prepared in the

same manner as in Example 1 except for using carbazole (CR1) as a polymerization photosensitizer instead of NEDC (C1).

- Fabricability of the resulting liquid
- 5 composition was evaluated using JSC-2000 in the same manner as in Example 1. This resin composition was not cured at all by irradiation at a dose of 100 mJ/cm² or even at a dose of 500 mJ/cm².

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Table 1

	Cationocally polymerizable compound (wt%)		Cationic photoinitiator (wt%)		Cationic photopolymerization (wt%)		Cure depth at a dose of 100 mJ/cm ² (μ m)	Minimum sensitivity (mJ/cm ²)	Young's modulus (kg/mm ²)
	A1	A2	B1	B2	C1	C2			
Example 1	A1	64.5	B1	5.0	C1	0.5	300	16	190
	A2	30.0							
Example 2	A1	95.0	B1	3.0	C1	2.0	280	18	210
Example 3	A1	48.0	B1	3.0	C1	1.0	310	16	180
	A2	48.0							
Example 4	A1	47.0	B1	5.0	C1	0.5	280	15	190
	A2	47.0							
Example 5	A1	48.2	B1	3.0	C1	0.5	310	18	180
	A2	48.3							
Comparative Example 1	A1	97.0	B1	3.0	-		80	56	80
Comparative example 2	A1	95.0	B1	3.0	CR1	2.0	Did not cure	Did not cure	

- Cationically polymerizable compound
- A1: 3,4-epoxycyclohexylmethyl-3',4'-
epoxycyclohexanecarboxylate
- A2: neopentyl glycol diglycidyl ether
- 5 A3: bis(3,4-epoxycyclohexylmethyl)adipate
- Cationic photoinitiator
- B1: bis 4-(di(4-(2-
hydroxyethyl)phenyl)sulfonio)phenyl]sulfide
bishexafluoroantimonate
- 10 Cationic photopolymerization photosensitizer used in
the present invention
- C1: 9,9'-diethyl-3,3'-dicarbazole (NEDC)
- Carbazole compound used in Comparative Example 2
- CR: carbazole

15

Curability for ensuring the fabrication and
Young's modulus for evaluating mechanical strength were
measured as described below.

(Evaluation of curability)

- 20 The photo curable liquid resin composition was
selectively irradiated using a photofabrication
apparatus "Solid Creator JSC-2000" (manufactured by
SONY Corp.) equipped with an Ar ion laser (wavelength:
351nm, 365nm) as a light source with a laser spot
- 25 diameter of 200 μ m and a laser power of 100 mW at the
irradiation surface (liquid surface) while changing the
scanning speed from 100 to 1,000 mm/second to measure
the thickness (cure depth) of the cured layer of the
resin composition. Minimum sensitivity was defined by
- 30 plotting the cure depth corresponding to the logarithm
of the dose and extrapolating the dose at which the
cure depth became 0. As the minimum sensitivity is
smaller, curability of the resin was judged to be

superior. When the scanning speed was 500 mm/second, the dose became 100 mJ/cm² since the irradiated area per 1 second was 1 cm². The thickness of the cured layer at this dose was determined as the cure depth at a dose of 5 100 mJ/cm². The determination is further elucidated in Figure 1.

Figure 1 is a schematic diagram showing a method of determining the minimum sensitivity from the cure depth of the cured products formed from the 10 photocurable compositions prepared in Examples and Comparative Examples.

Measurement of Young's modulus

(1) Preparation of test specimen:

15 The photo curable liquid resin composition was selectively irradiated using Solid Creator JSC-2000 with a laser power of 100 mW at the irradiation surface (liquid surface) and a scanning speed at which the cure depth of each composition was 0.3 mm to form a cured 20 resin layer (thickness: 0.20 mm). This step was repeated to fabricate a JIS-1A dumbbell specimen.

(2) Measurement:

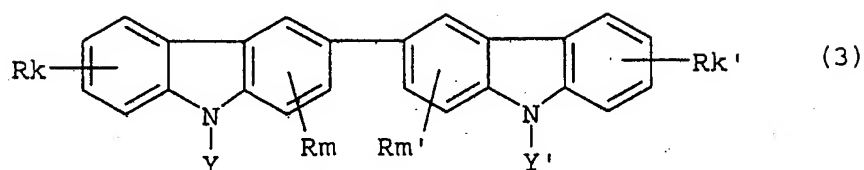
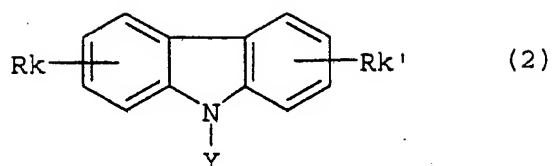
25 Young's modulus was measured from a tangent on the graph showing the initial strain and stress of the test specimen when stretched at a tensile rate of 1 mm/min. in a thermo-hygrostat (temperature: 80°C, relative humidity: 95%).

Effect of the Invention

The photo curable liquid resin composition of the present invention exhibits excellent photocurability (photocuring rate) and can produce a cured product having high mechanical strength having a Young's modulus of higher than 100 kg/cm², more in particular between 110-500 kg/cm². In particular, photofabricated cured products such as prototypes of machine parts for which mechanical strength is required can be prepared from the photo curable liquid resin composition by utilizing a three-dimensional photofabrication apparatus using a near ultraviolet light having a wavelength of 350 nm or more.

C L A I M S

1. A photo curable liquid resin composition comprising (A) a cationically polymerizable organic compound, (B) a cationic photoinitiator, and (C) a cationic photopolymerization photosensitizer comprising at least one compound comprising at least one N-substituted carbazole group.
2. Resin composition according to claim 1 wherein component (A) comprises at least one compound having a glycidyl group, cyclohexene oxide group or oxetanyl group.
3. Resin composition according to any one of claims 1-2, wherein component A comprises one or more compounds having molecular weights between 50-20,000.
4. Resin composition according to any one of claims 1-3, wherein the composition comprises relative to components A-C
60-99.9 wt.% of component A
0.1-20 wt.% of component B
0.001-20 wt.% of component C
5. Resin composition according to any one of claims 1-4, wherein component C comprises a compound having 1-10 carbazole groups.
6. Resin composition according to any one of claims 1-5, wherein the carbazole comprising compound has a molecular weight between 180-2000.
7. Resin composition according to any one of claims 1-6, wherein component C comprises at least one carbazole compound as shown by formula (2) or (3)

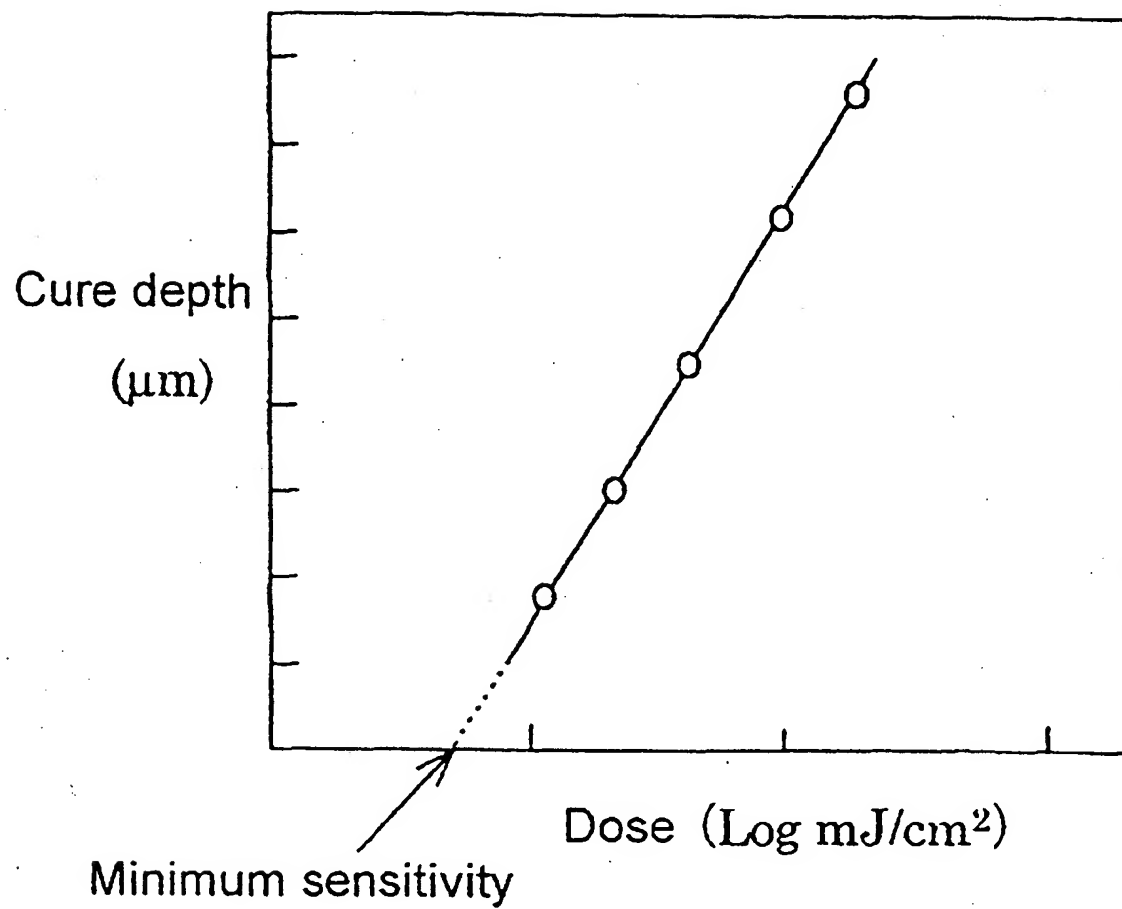


- wherein R independently represents a fluorine atom, chlorine atom, bromine atom, a hydroxyl group, mercapto group, nitro group, or a C₁-C₁₈ monovalent organic group, k and k' independently represent integers from 0-4, m and m' independently represent integers from 0-2, and Y and Y' independently represent a C₁-C₁₈ monovalent organic group.
- 5 8. Resin composition according to any one of claims 1-7, wherein the composition further comprises radically polymerizable organic compounds and radical photoinitiators.
 - 15 9. Resin composition according to any one of claims 1-8, wherein the composition has a viscosity at 25°C of 50-2000 cps.
 - 20 10. Method for making a three-dimensional object by providing (1) a thin layer of the resin composition according to any one of claims 1-9 on a support and (2) selectively irradiating a part of said layer to cure the resin, (3) providing a further thin layer of said resin (4) selectively

irradiating a part of said layer to cure the resin and (5) repeating steps (3) and (4) to obtain the object, and optionally apply further treatment steps as to obtain a useable object.

- 5 11. Method according to claim 10 wherein the curing is achieved by irradiation with near UV light having a wavelength of 350 nm or more.
12. Method according to any one of claims 10-11, wherein the curing is achieved by irradiating
- 10 with an Argon ion laser having main wavelength at 351 and 365 μm .
13. A photofabricated cured product prepared by photopolymerization of the photo curable liquid resin composition according to any one of claims
- 15 1-9, or obtained by the method according to any one of claims 10-12.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 00/00101

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/3417 C08G59/68 C08G65/10 C08F2/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C08K G03F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	WO 98 12232 A (NIPPON SODA CO ; TAKAHASHI EIJI (JP)) 26 March 1998 (1998-03-26) the whole document ---	1-7,9,13 8,10-12
X A	DATABASE WPI Section Ch, Week 199207 Derwent Publications Ltd., London, GB; Class A18, AN 1992-053958 XP002139717 -& JP 04 001205 A (CANON KK), 6 January 1992 (1992-01-06) abstract --- -/--	1-7,9,13 10-12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Int. Patent Application No
PCT/NL 00/00101

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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